

Viscoelastic Acoustic Response of Layered Polymer Films at Fluid-Solid Interfaces: Continuum Mechanics Approach

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Abstract

We have derived the general solution of a wave equation describing the dynamics of two-layer viscoelastic polymer materials of arbitrary thickness deposited on solid (quartz) surfaces in a fluid environment. Within the Voigt model of viscoelastic element, we calculate the acoustic response of the system to an applied shear stress, i.e. we find the shift of the quartz generator resonance frequency and of the dissipation factor, and show that it strongly depends on the viscous loading of the adsorbed layers and on the shear storage and loss moduli of the overlayers. These results can readily be applied to quartz crystal acoustical measurements of the viscoelasticity of polymers which conserve their shape under the shear deformations and do not flow, and layered structures such as protein films adsorbed from solution onto the surface of self-assembled monolayers.

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1. INTRODUCTION

The analysis of viscoelastic behavior of biomolecular films at fluid-fluid and fluid-solid interfaces is a very active interdisciplinary field and a “hot” topic in the physics of modern surface phenomena, which has many possible applications [1-13]. Particular attention is focused now on macromolecular multilayer assemblies such as polymer “brush” films [2], adsorbed protein layers [3,6,7-10] as well as on self-assembled monolayers (SAM) [1,6,9]. The importance of studying such biomolecular sandwich structures arises from the prospect of their use as molecular biosensors and for medical and environmental applications [3,6,8-10]. The mechanical properties of these structures can be determined with high accuracy from the frequency response of a quartz oscillator in contact with them [6,8-14]. An increasing number of theoretical and experimental investigations of quartz crystal microbalances (QCM:s) functioning in liquid environments have opened a possibility for *in situ* measurements of biomolecular assemblies and for a quantitative interpretation of their viscoelastic response [7-17]. Among theoretical methods, a continuum mechanics approach is often used. In contrast to the electrical circuit method or a transmission line analysis ([4], [5], for a review see also [8] and Refs. [13,15] therein), this approach is directly linked to the physical description of the system and provides a clear connection between measured characteristics and material parameters. Within continuum mechanics the mechanical properties of viscoelastic materials are usually related to energy storage and dissipation processes resulting from the balance between an applied stress and the ensuing relaxation processes in the material. The experimental conditions determine the amount of stress, whereas the relaxation rates are intrinsic properties of the material [2,7,18,19].

The simplest way of accounting for the mechanical properties of a visco-elastic material is to introduce a shear viscosity coefficient η and a shear elasticity modulus μ within one of two basic models due to (i) Maxwell and (ii) Voight. In contrast to the Maxwell model, the characteristics of the so called Voight element used in that model is the following: It does not describe a flow at a steady rate; the viscoelastic element is described by complex shear

modulus, real part of which (the storage modulus) is independent of frequency whereas its imaginary one (the loss modulus) increases linearly with frequency [19]. In addition to the Maxwell and Voight models various combinations of them have been used (for a review, see Refs [14,18,2,7]).

The Maxwell model is usually applied to polymer solutions which can — at least for low shear rates — demonstrate purely liquid-like behavior. The Voight model is applicable for polymers which conserve their shape and do not flow [18,19].

In the present study we analysed, within the continuum mechanics approach, the viscoelastic response of two polymer layers covering a quartz plate subject to shear deformations. The viscoelastic material was modelled as a Voight element, with its parallel arrangement of a spring and a dashpot. Even this relatively simple theoretical model has allowed us to demonstrate the most important consequences of adsorbate viscoelasticity in terms of a deviation from the Sauerbrey relation [4] relevant for a gas phase environment and ultrathin layers. We have also been able to elucidate the role of viscous loading when the oscillator is immersed in a bulk liquid.

2. MODEL

We consider the case of two viscoelastic layers covering the surface of a piezo-electric plate oscillating in a pure shear mode in a bulk liquid. We derive here a general solution of the corresponding wave equation and analyze it using “no-slip” boundary conditions. In our model the result of Reed *et al.* [16] emerges as a special case (i.e., when both layers are equivalent, and the upper (Newtonian) liquid has a vanishing density).

The geometry of the model system is shown in Fig. 1. We treat the quartz plate (index ‘0’) as a harmonic oscillator whose resonant frequency in vacuum [4, 5, 10-17], f_0 , is

$$f_0 = \frac{\ell_0}{2h_0} \sqrt{\frac{\mu_0}{\rho_0}}.$$

Hence f_0 is a function of the thickness h_0 of the quartz plate, its density ρ_0 , and its elastic shear modulus μ_0 .

The quartz slab is treated as a loss-less generator when it operates in vacuum (or a gaseous environment). It is known that mass loading changes the resonant frequency of the oscillator. For sufficiently thin non rigid overlayers, the shift of the resonant frequency is proportional to the added mass only [4],

$$\Delta f \approx f_0 \Delta m ,$$

and the energy dissipation due to viscous losses is then negligibly small [6], i.e. such a layer demonstrates a solid-like response in vacuum or gaseous experimental conditions.

In the opposite case of total immersion of the quartz slab into a liquid (in general into a viscoelastic medium) both the energy dissipation due to the oscillatory motion excited in the interfacial solid-liquid region, and the resonant frequency shift, are functions of the overlayer viscosity (elasticity) and density [13]. Our results show that even very thin viscoelastic films can dissipate a significant amount of energy when the quartz plate with overlayers oscillates in the liquid phase. The energy dissipation in QCM experiments can be obtained by measuring the dissipation factor D which is inversely proportional to the decay time constant [6]

$$D = \frac{1}{\pi f \tau} ,$$

where f is the resonant frequency. For a purely viscous bulk liquid, it has been shown that the resonance frequency shift [15] and the dissipation factor shift [5,6] depend on the density and shear viscosity of the liquid.

Let us consider a viscoelastic overlayer medium within the Voight scheme of using a viscoelastic element (Fig. 2) which consists of a spring and a dashpot in parallel. When a shear stress σ_{xy} is applied to a Voight element, the elastic response of the spring and the dashpot viscous resistance contribute to the stress/strain relation as follows:

$$\sigma_{xy} = \mu \frac{\partial u_x(y, t)}{\partial y} + \eta \frac{\partial v_x(y, t)}{\partial y} . \quad (1)$$

Here u_x is the displacement in the x direction and the corresponding velocity is v_x ; μ is the elastic shear modulus and η is the shear viscosity of the overlayer, respectively.

The wave equation for bulk shear waves propagating in a viscoelastic medium is [16]:

$$\mu^* \frac{\partial^2 u_x(y, t)}{\partial y^2} = -\rho \omega^2 u_x(y, t), \quad (2)$$

where $\mu^* \equiv \mu' + i\mu'' = \mu + i\omega\eta$ is a complex shear modulus. The general solution of Eq. (2) can be written as

$$u_x(y, t) = (C_1 e^{-\xi y} + C_2 e^{\xi y}) e^{i\omega t}, \quad (3)$$

where $\xi = \alpha + ik$ contains a decay constant α ,

$$\alpha = \frac{1}{\delta} \sqrt{\frac{\sqrt{1+\chi^2} - \chi}{1+\chi^2}} \quad (4)$$

and a wave number k ,

$$k = \frac{1}{\delta} \sqrt{\frac{\sqrt{1+\chi^2} + \chi}{1+\chi^2}} \quad (5)$$

$$\chi = \frac{\mu}{\eta\omega}, \quad \delta = \sqrt{\frac{2\eta}{\rho\omega}}.$$

Here we introduce the viscoelastic ratio χ as the ratio between real part (storage modulus) and imaginary one (loss modulus) of complex shear modulus and a viscous penetration depth δ , respectively. The coefficients C_1 and C_2 in Eq. (3) can be determined from the appropriate boundary conditions.

3. “NO-SLIP” CONDITIONS

The so-called “no-slip” boundary condition at the solid-overlayer interface ($y = 0$) corresponds to a continuous variation of the displacement u_x and of the shear stress σ_{xy} across the interface. These quantities are related as follows,

$$v_x = \frac{\partial u_x}{\partial t}, \quad \sigma_{xy} = \mu_1 \frac{\partial u_x}{\partial y} + \eta_1 \frac{\partial v_x}{\partial y},$$

$$\sigma_{xy} = \mu_0 \frac{\partial q_x}{\partial y}, \quad q_x = u_x. \quad (6)$$

Here q_x correspondes to the component of quartz substrate displacement vector, μ_0 is the substrate elastic shear modulus.

For the two-layer system we have a continuous variation at the surfaces $y = h_j$ of the velocities $v_x^{(i)}$ and the shear stresses σ_{ik}^i . Hence at $y = h_1$ we have

$$\begin{aligned} n_k \sigma_{ik}^{(1)} &= n_k \sigma_{ik}^{(2)}, \\ v_x^{(1)} &= v_x^{(2)}, \quad v_z^{(1)} = v_z^{(2)} = 0, \\ \sigma_{ik}^{(1)} &= -p_1 \delta_{ik} + \eta_1 \left(\frac{\partial v_i^{(1)}}{\partial x_k} + \frac{\partial v_k^{(1)}}{\partial x_i} \right) + \mu_1 \left(\frac{\partial u_i^{(1)}}{\partial x_k} + \frac{\partial u_k^{(1)}}{\partial x_i} \right), \\ \sigma_{ik}^{(2)} &= -p_2 \delta_{ik} + \eta_2 \left(\frac{\partial v_i^{(2)}}{\partial x_k} + \frac{\partial v_k^{(2)}}{\partial x_i} \right) + \mu_2 \left(\frac{\partial u_i^{(2)}}{\partial x_k} + \frac{\partial u_k^{(2)}}{\partial x_i} \right), \end{aligned} \quad (7)$$

The no-slip boundary condition at $y = h_2$ gives:

$$\begin{aligned} n_k \sigma_{ik}^{(2)} &= n_k \sigma_{ik}^{(3)}, \\ v_x^{(2)} &= v_x^{(3)}, \quad v_z^{(2)} = v_z^{(3)} = 0, \\ \sigma_{ik}^{(2)} &= -\rho_2 \delta_{ik} + \eta_2 \left(\frac{\partial v_i^{(2)}}{\partial x_k} + \frac{\partial v_k^{(2)}}{\partial x_i} \right) + \mu_2 \left(\frac{\partial u_i^{(2)}}{\partial x_k} + \frac{\partial u_k^{(2)}}{\partial x_i} \right), \\ \sigma_{ik}^{(3)} &= -\rho_3 \delta_{ik} + \eta_3 \left(\frac{\partial v_i^{(3)}}{\partial x_k} + \frac{\partial v_k^{(3)}}{\partial x_i} \right). \end{aligned} \quad (8)$$

Finally, at the free surface, $y = h_3$, the boundary condition is

$$\eta_2 \frac{\partial v_x^{(3)}}{\partial y} = 0. \quad (9)$$

A general solution for the wave equation (2) with boundary conditions (6-9) can be written as

$$v_x = v_0 \frac{e^{2\xi_1 y} + A e^{2\xi_1 h_1}}{e^{\xi_1 y} (1 + A e^{2\xi_1 h_1})}, \quad (10)$$

$$A = \frac{\kappa_1 \xi_1 (1 + l e^{2\xi_2 \Delta h_1}) - \kappa_2 \xi_2 (1 - l e^{2\xi_2 \Delta h_1})}{\kappa_1 \xi_1 (1 + l e^{2\xi_2 \Delta h_1}) + \kappa_2 \xi_2 (1 - l e^{2\xi_2 \Delta h_1})}, \quad l = \frac{\kappa_2 \xi_2 + \kappa_3 \xi_3 \tanh(\xi_3 \Delta h_2)}{\kappa_2 \xi_2 - \kappa_3 \xi_3 \tanh(\xi_3 \Delta h_2)} \quad (11)$$

$$\Delta h_1 = h_2 - h_1, \quad \Delta h_2 = h_3 - h_2, \quad (12)$$

$$\xi_{1,2} = \sqrt{-\frac{\rho_{1,2}\omega^2}{\mu_{1,2}^*}} = \alpha_{1,2} + ik_{1,2}, \quad \xi_3 = \sqrt{i\frac{\rho_3\omega}{\eta_3}} \quad (13)$$

$$\kappa_{1,2} = \eta_{1,2} - \frac{i\mu_{1,2}}{\omega} \equiv \frac{\mu_{1,2}^*}{i\omega}, \quad \kappa_3 = \eta_3. \quad (14)$$

The shift in resonance frequency Δf and dissipation factor ΔD are obtained, respectively, from the imaginary and real parts of the β -function [6]:

$$\begin{aligned} \Delta f &= \text{Im} \left(\frac{\beta}{2\pi\rho_0 h_0} \right), \\ \Delta D &= -\text{Re} \left(\frac{\beta}{\pi f \rho_0 h_0} \right) \end{aligned} \quad (15)$$

where

$$\beta = \kappa_1 \xi_1 \frac{1 - Ae^{2\xi_1 h_1}}{1 + Ae^{2\xi_1 h_1}}. \quad (16)$$

Below we analyze the general results expressed in Eqs. (10-16) in the limit cases of thin and thick viscoelastic layers deposited on the quartz oscillator surface when the oscillator operates (i) in vacuum (or a gaseous environment) and (ii) in a bulk liquid.

4. RESULTS

4.1. Viscoelastic layer in vacuum

From general solution for the wave equation (10) it follows that the overlayer thickness always appears as a dimensionless $h\xi$ combination. Thus, the limit cases of "thin"/"thick" film correspond to the situations wheather the film thickness is much smaller/greater in comparison with the reverse value of a decay α constant and the propagation k constant which is reduced to the following criteria:

in the 'thin film' approximation $h/\delta \ll \sqrt{\chi/2}$ for $\chi > 1$ and $h/\delta \ll 1 - \chi/2$ for $\chi < 1$;

'thick layer' correspondes to inequalities $h/\delta \gg \chi\sqrt{2\chi}$ for $\chi > 1$ and $h/\delta \gg 1 + \chi/2$ for $\chi < 1$.

For pure viscous film this criterium corresponds to the well-known ratio between a film thickness h and a viscous penetration depth δ : in the thin layer approximation $h/\delta \ll 1$ [20].

Let us consider the solution of wave equation for one viscoelastic layer on the QCM surface when the system oscillates in vacuum (or in a gas). In such case, from general expressions (11-16) we get for β -function:

$$\beta = -\kappa\xi \tanh(\xi h). \quad (17)$$

By a series expansion on $h\alpha \ll 1$ and $hk \ll 1$ in special case of thin overlayer, we find from (15) and (17) that

$$\Delta f \approx -\frac{1}{2\pi\rho_0 h_0} h \rho \omega \left(1 - \frac{2h^2}{3\delta^2(1+\chi^2)}\right) \quad (18)$$

$$\Delta D \approx \frac{2h^3 \rho \omega}{3\pi f \rho_0 h_0} \frac{\chi}{\delta^2(1+\chi^2)}, \quad \chi = \frac{\mu}{\eta \omega}, \quad \delta = \sqrt{\frac{2\eta}{\rho \omega}} \quad (19)$$

It is clear from Eqs. (18) and (19) that to linear order in the (small) thickness, the dissipation factor vanishes, while the frequency shift is a function of oscillation frequency and mass of the layer. This is the well-known Sauerbrey relation for the loss-less quartz oscillator overlayered with a thin film:

$$\Delta f_{Sauerbrey} = -\frac{f_0}{\rho_0 h_0} \Delta m, \quad \Delta m \equiv \rho h$$

$$\Delta D = 0$$

The viscosity and elasticity of the overlayer only appears in the third order approximation with respect to thickness. For sufficiently thin layers, it leads to a small correction to the Sauerbrey relation which can be hardly observed experimentally.

In the opposite case of a "thick" viscoelastic layer ($h\alpha \gg 1$, $hk \gg 1$) we readily find that $\beta \approx -\kappa\xi$ and that

$$\Delta f \approx -\frac{1}{2\pi\rho_0 h_0} \sqrt{\frac{\rho}{2}} \left\{ \eta\omega \sqrt{\frac{\sqrt{\mu^2 + \eta^2\omega^2} + \mu}{\mu^2 + \eta^2\omega^2}} - \mu \sqrt{\frac{\sqrt{\mu^2 + \eta^2\omega^2} - \mu}{\mu^2 + \eta^2\omega^2}} \right\} \quad (20)$$

$$\Delta D \approx \frac{1}{\pi f \rho_0 h_0} \sqrt{\frac{\rho}{2}} \left\{ \eta\omega \sqrt{\frac{\sqrt{\mu^2 + \eta^2\omega^2} - \mu}{\mu^2 + \eta^2\omega^2}} + \mu \sqrt{\frac{\sqrt{\mu^2 + \eta^2\omega^2} + \mu}{\mu^2 + \eta^2\omega^2}} \right\}. \quad (21)$$

The shift of resonance frequency (20) and the dissipation factor changes (21) are functions of film viscoelasticity and can be measured in QCM experiments.

In the viscous limit ($\mu \rightarrow 0$) we recover the result of Ref. [15] for the frequency shift,

$$\Delta f \approx -\frac{1}{2\pi\rho_0 h_0} \sqrt{\frac{\rho\eta\omega}{2}}, \quad (22)$$

and the result of Refs. [5,6] for the shift of the dissipation factor,

$$\Delta D \approx \frac{1}{\rho_0 h_0} \sqrt{\frac{2\rho\eta}{\omega}}. \quad (23)$$

4.2. Viscoelastic layers in a bulk liquid

Let us consider two thin viscoelastic overlayers of thickness h_j ($j = 1, 2$) under a bulk Newtonian liquid for which its thickness Δh_2 satisfies the inequality $\xi_3 \Delta h_2 \gg 1$. In this case we may expand the expression for β and keep only terms linear in $h_j \alpha_j \ll 1$ and $h_j k_j \ll 1$. The acoustic response of the QCM with the thin viscoelastic layers immersed in a Newtonian bulk liquid (index “3”):

$$\Delta f \approx -\frac{1}{2\pi\rho_0 h_0} \left\{ \frac{\eta_3}{\delta_3} + \sum_{j=1,2} \left[h_j \rho_j \omega - 2h_j \left(\frac{\eta_3}{\delta_3} \right)^2 \frac{\eta_j \omega^2}{\mu_j^2 + \omega^2 \eta_j^2} \right] \right\} \quad (24)$$

$$\Delta D \approx \frac{1}{2\pi f \rho_0 h_0} \left\{ \frac{\eta_3}{\delta_3} + \sum_{j=1,2} \left[2h_j \left(\frac{\eta_3}{\delta_3} \right)^2 \frac{\mu_j \omega}{\mu_j^2 + \omega^2 \eta_j^2} \right] \right\}. \quad (25)$$

From Eqs. (24) and (25) it follows that for ultrathin films the contribution of the film is small in comparison with the bulk liquid acoustic response $\Delta f \sim -\eta_3/\delta_3$, $\Delta D \sim \eta_3/\delta_3$. However, a thin layer with a finite thickness will demonstrate a different acoustic response depending on the ratio between the viscosity and the elasticity of the film.

To make a picture more clear, let start from only one thin viscous overlayer under a bulk Newtonian liquid. For a purely viscous overlayer, the resonant frequency shift depends on a bulk η_3/δ_3 term and the difference between the film mass contribution ($h_1\rho_1\omega$) and its viscous contribution ($\sim h_1/\eta_1$) multiplied by factor $(\eta_3/\delta_3)^2$ due to the penetration of acoustical vibrations through the adsorbed layer into a bulk liquid and corresponding energy loss due to the viscous dissipation. The dissipation factor (25) is determined by properties of bulk liquid.

We found, that even in this simple case there exists an important for experiments situation when the resonance frequency shift of layered system (24) is equal to a bulk liquid response only but not of adsorbed layer one. This occurs for such a relationship between viscosities and densities of the media, i.e. $\eta_3\rho_3 = \eta_1\rho_1$, at which the 'mass response' will compensate the viscous one. We can explain this subtraction as a result of damping and reflection of travelling acoustic waves in a layered medium with different density and viscosity of the layers.

In the opposite case, for purely elastic film ($\eta_1 \rightarrow 0$) one can find that only the dissipation factor change depends on the film elasticity ($\Delta D \sim h_1/\mu_1$), while the frequency shift contains the mass response of the film ($\Delta f \sim h_1\rho_1$) but not the elastic one. It is easy to see that for a gaseous environment when η_3 tends to zero, we recover the Sauerbrey relation (see also the next paragraph). Thus, it is essential to note that the viscous bulk loading of the adsorbed layer leads to the appearance of a viscous (viscoelastic) contribution of the layer and hence opens up a possibility for the corresponding QCM measurements to determine the viscoelastic parameters of the overlayer(s) when the resonator oscillates in a bulk liquid.

In Figs. 3 - 6 we have presented the calculated change in resonance frequency and in the dissipation factor as a function of the viscoelastic film thickness h_1 for a given value of the layer viscoelasticity ($\mu_1 = 10^4 - 10^5 \text{ N/m}^2$, $\eta_1 = 0.01 \text{ Ns/m}^2$, $\rho_1 = 10^3 \text{ kg/m}^3$) when a quartz plate oscillates with frequency $f_0 = 5 \cdot 10^6 \text{ Hz}$ in bulk water ($\rho_3 = 10^3 \text{ kg/m}^3$, $\eta_3 = 10^{-3} \text{ kg/m}^3$).

In real experimental situation, not only changes of the thickness of adsorbed layer must be taken into account. Variations of $\Delta f(\mu, \eta)$ and $\Delta D(\mu, \eta)$ during the adsorption can be of crucial importance as viscoelastic parameters of the adsorbate can also vary during the process of coverage.

To illustrate the variation of Δf and ΔD with the viscoelastic layer parameters μ and η , we have shown in Figs. 7 - 8 the results of a numerical simulation of the model for the thin viscoelastic layer of a given thickness $h_1 = 10^{-6}$ m and density $\rho_1 = 10^3$ kg/m³, when a generator oscillates with frequency $f_0 = 10^7$ Hz in bulk water. The resulting nonmonotonic behavior of $\Delta f(\mu, \eta)$ and $\Delta D(\mu, \eta)$ gives the evidence for key contribution of viscoelasticity in complex polymer adsorbed layers dynamics in a liquid medium.

5. CONCLUSIONS

We have found a general solution of the wave equation describing the propagation and decay of shear waves in layered viscoelastic medium in contact with a quartz surface. This sandwich structure can be used to model the response of viscoelastic polymer and biomolecular films such as polymer “brush” films or proteins adsorbed from solution onto a solid substrate modified by SAM covering before adsorption. Our results can be summarized as follows.

(i) We have analysed both “thin” and “thick” layer acoustical responses. These two limit cases correspond to whether the film thickness is much smaller/greater in comparison with the viscous penetration depth $\delta = \sqrt{2\eta/\rho\omega}$ and the viscoelastic ratio $\chi = \mu/\eta\omega$.

(ii) To elucidate the validity of the Sauerbrey “ideal mass thin layer” response, we have calculated the “thin” viscoelastic layer resonance frequency shift. We found that the “ideal mass layer” response corresponds to a purely elastic behavior of the Voight element, i.e. to an element with zero shear viscosity. Due to the viscosity of the adsorbed layer, the acoustical response of the system becomes to diverge with an “ideal mass thin layer” behavior when the ratio of the film thickness h and the penetration depth δ tends to 1/2 (for small values

of viscoelastic ratio $\chi \ll 1$).

(iii) In case of a "thick" viscoelastic medium we found the shifts in resonance frequency and dissipation factor as functions of the ratio of storage and loss moduli. Using Eqs. (20) and (21) it is possible to calculate these moduli using data from the corresponding acoustic experiments.

(iv) We derived the general expression for the acoustic response of two viscoelastic layers of arbitrary thickness covering the surface of a quartz oscillator when it is immersed in a Newtonian liquid. This result allows us to analyze the dynamics of a layered medium with arbitrary layer thicknesses and with a viscoelastic ratio which can vary during the coverage.

We have presented analytical expressions for the resonance frequency shift and the dissipation factor response of thin viscoelastic layers in contact with a liquid. The analysis showed that in contrast to oscillations in vacuum or in a gas environment, even a thin viscoelastic layer will dissipate a significant amount of energy. We have therefore also shown that a viscous bulk loading of the overlayer opens up the possibility to measure its viscoelastic properties from simultaneous measurements of Δf and ΔD using a QCM operating in a liquid environment.

The results of the model can readily be applied to quartz crystal acoustic measurements of adsorbed proteins which conserve their shape during adsorption and do not flow under shear deformation and of the polymer films far from the glass transition region.

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FIGURES

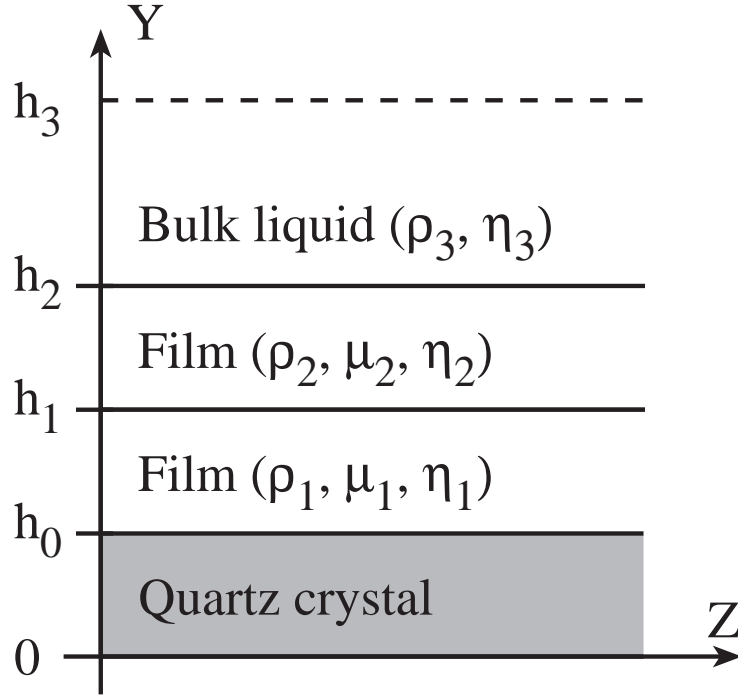


FIG. 1. Geometry of a quartz crystal microbalance (QCM) covered by a double-layer viscoelastic film. The QCM system oscillates in a bulk liquid.

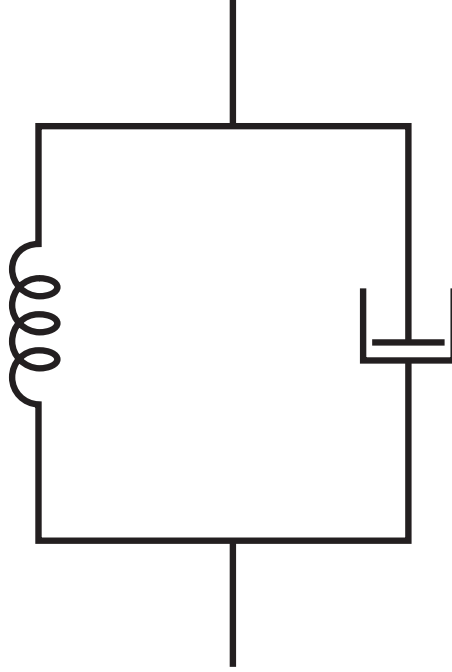


FIG. 2. Schematic depiction of the Voigt viscoelastic element.

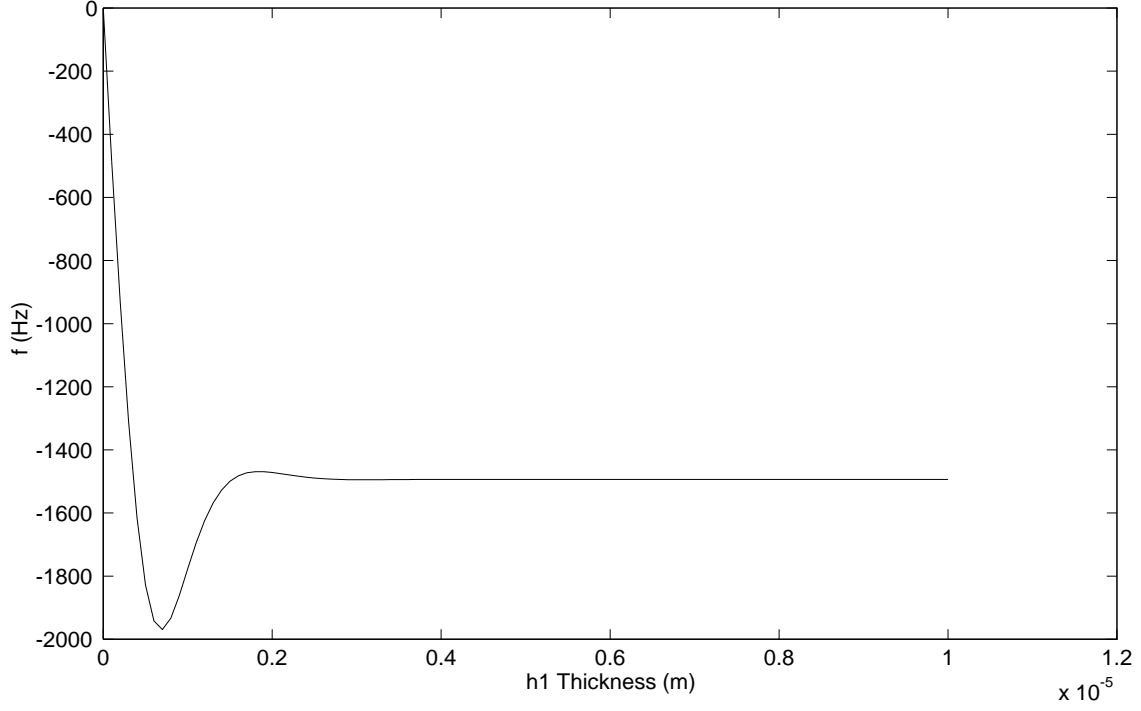


FIG. 3. Numerically calculated resonance frequency shift as a function of a viscoelastic overlayer thickness h_1 ; $\rho_1 = 1000 \text{ kg/m}^3$, $\eta_1 = 10^{-2} \text{ Ns/m}^2$, $\mu_1 = 10^4 \text{ N/m}^2$. The QCM oscillates in bulk water; $\rho_1 = 10^3 \text{ kg/m}^3$, $\eta_3 = 10^{-3} \text{ Ns/m}^2$, $f_0 = 5 \cdot 10^6 \text{ Hz}$.

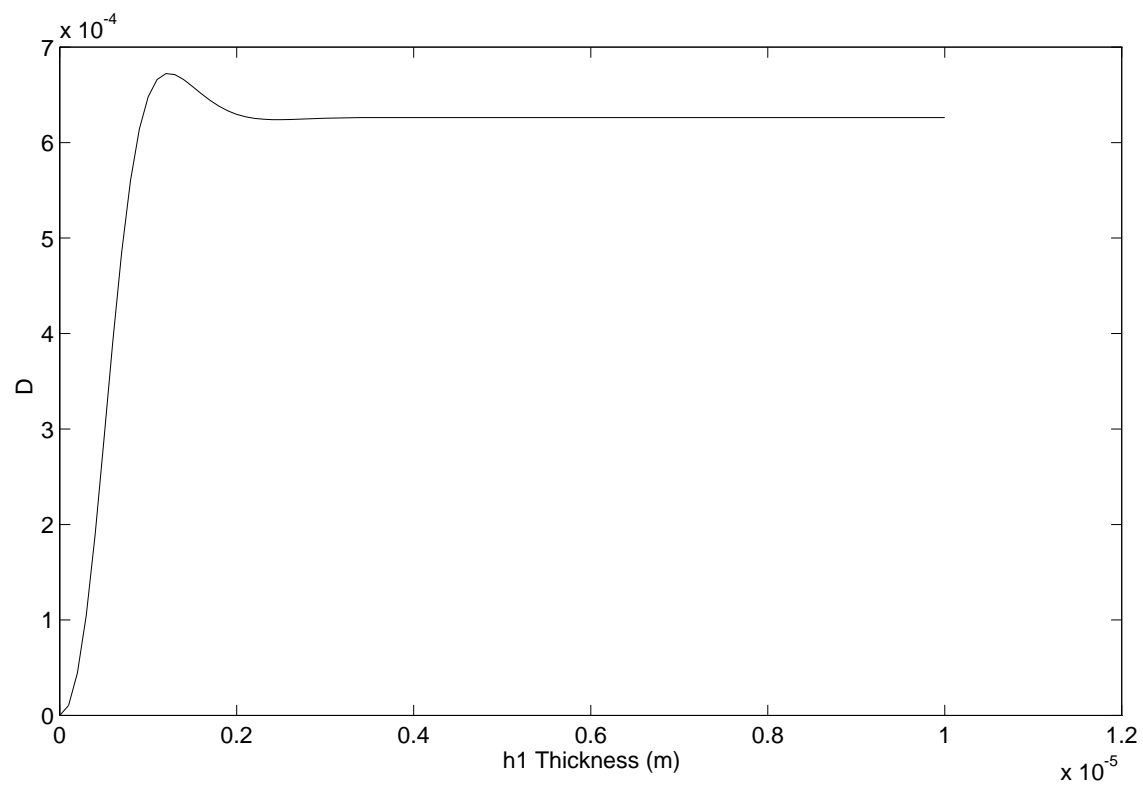


FIG. 4. Numerically calculated dissipation factor change as a function of a viscoelastic overlayer thickness (for the same parameters as in Fig. 3). The QCM oscillates in bulk water.

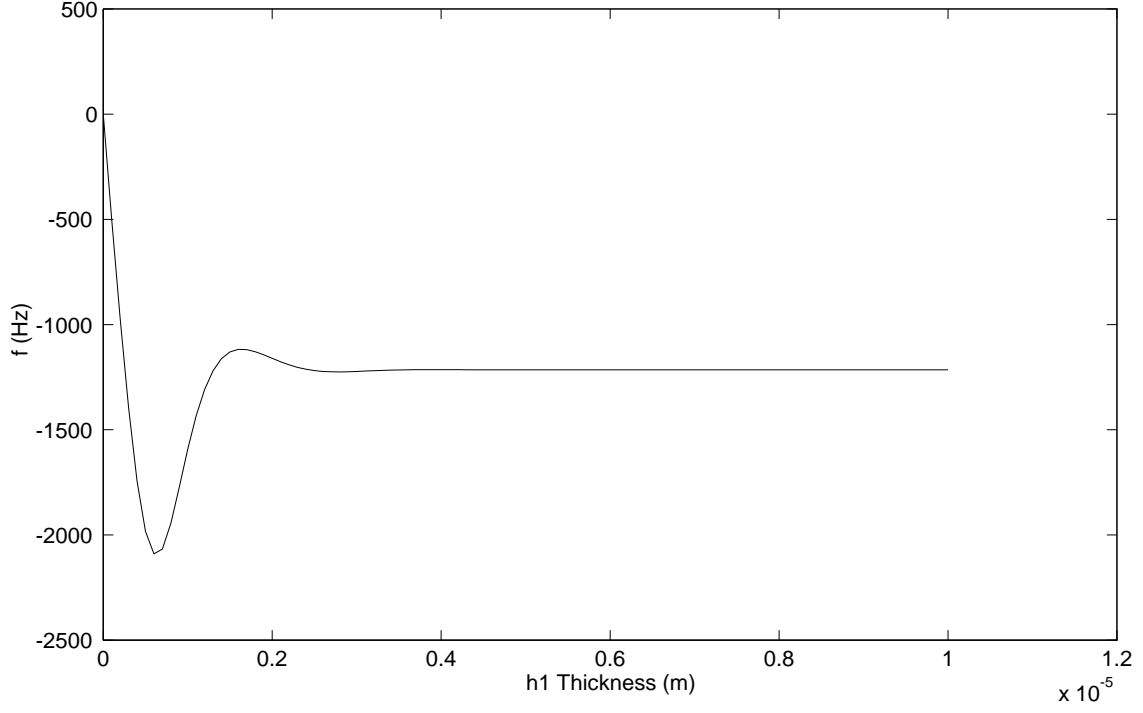


FIG. 5. Numerically calculated resonance frequency shift as a function of a viscoelastic overlayer thickness h_1 ; all the overlayer parameters are the same as in Fig.3 but with $\mu_1 = 10^5$ N/m². The QCM oscillates in bulk water; $f_0 = 5 \cdot 10^6$ Hz.

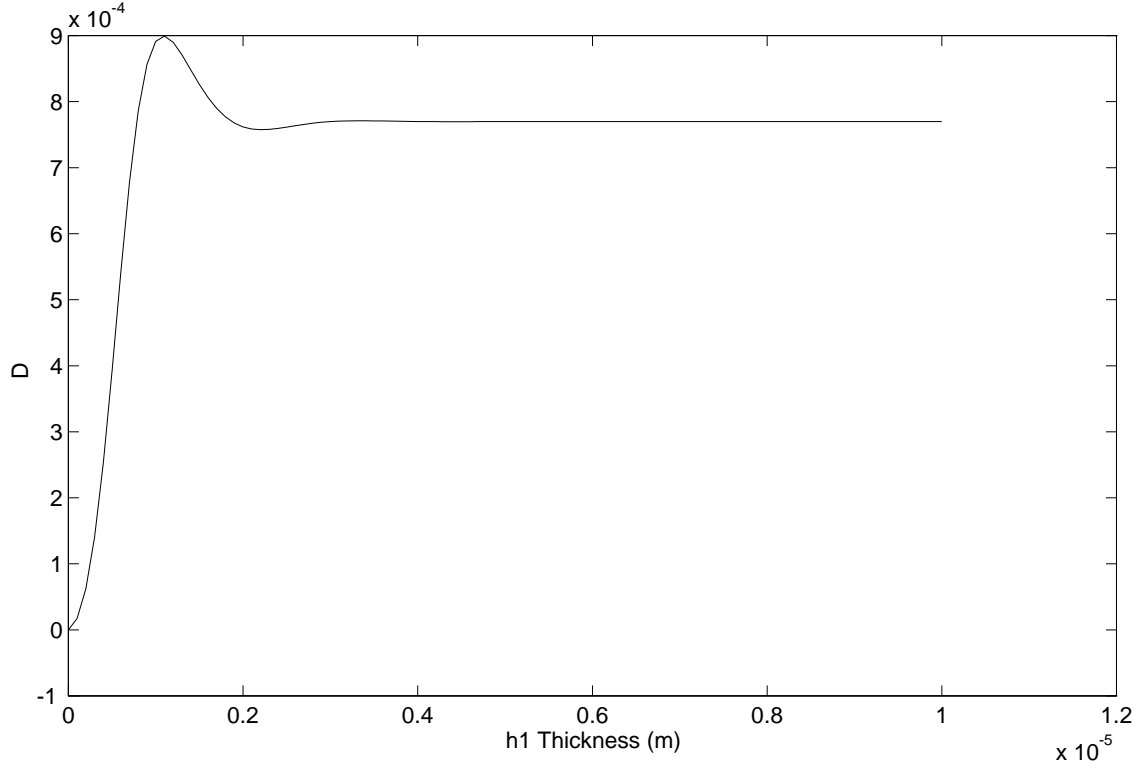


FIG. 6. Numerically calculated dissipation factor change as a function of a viscoelastic overlayer thickness (for the same parameters as in Fig. 5). The QCM oscillates in bulk water.

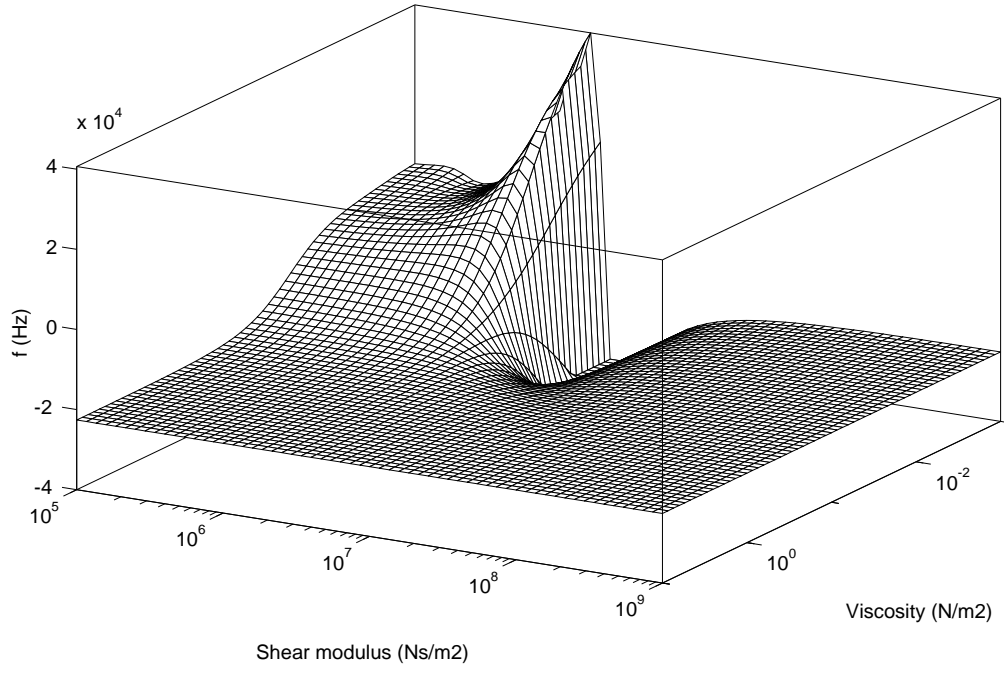


FIG. 7. Numerically calculated resonance frequency shifts as a function of the shear elasticity modulus μ_1 and the shear viscosity η_1 of the viscoelastic overlayer of thickness $h_1 = 10^{-6}$ m. The QCM oscillates in bulk water; $f_0 = 10^7$ Hz.

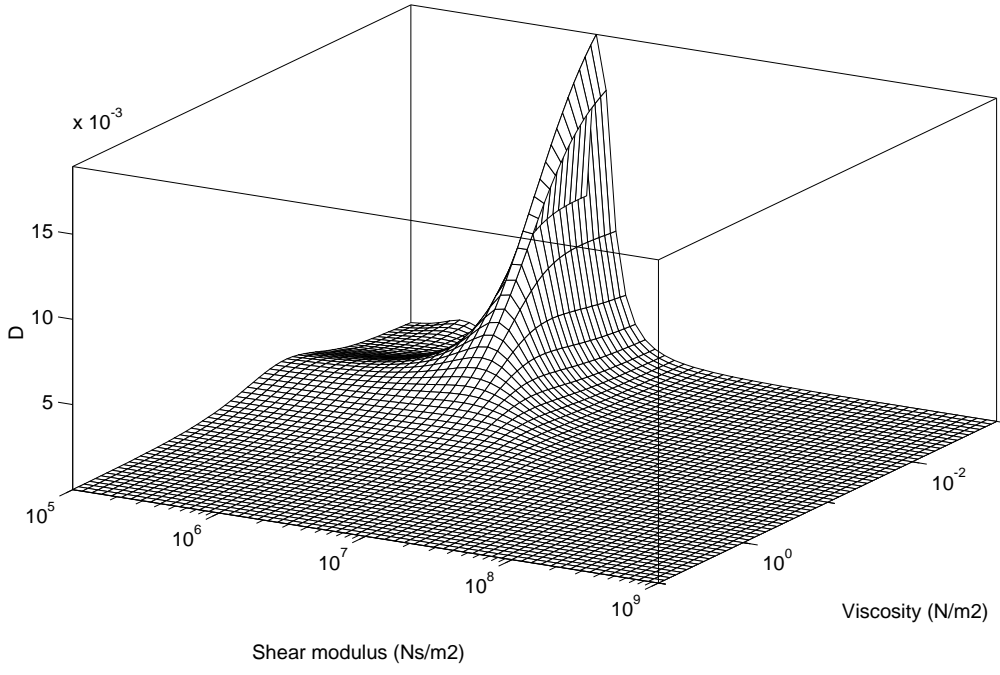


FIG. 8. Numerically calculated dissipation factor change as a function of the shear elasticity modulus μ_1 and the shear viscosity η_1 of the viscoelastic overlayer of thickness $h_1 = 10^{-6}$ m. The QCM oscillates in bulk water; $f_0 = 10^7$ Hz.